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(54) **PREPARATION OF PHTHALIC ANHYDRIDE BY GAS PHASE OXIDATION OF O-XYLENE**

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See application file for complete search history.

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(57) **ABSTRACT**

A process is described for preparing phthalic anhydride by catalytic gas phase oxidation of o-xylene, in, in a main reactor, a gaseous mixture of o-xylene and an oxygenous gas is passed through at least two reaction zones whose temperature can be controlled independently, and converted to a gaseous intermediate reaction product which comprises unconverted o-xylene, phthalic anhydride underoxidation products and phthalic anhydride, and the intermediate reaction product is introduced into a postreactor, wherein the temperature of the reaction zones in the main reactor is regulated in such a way that the concentration of unconverted o-xylene in the intermediate reaction product is at least 0.5% by weight. The process allows an increase in the overall yield of phthalic anhydride without or without significant deterioration in the product quality.

17 Claims, No Drawings

PREPARATION OF PHTHALIC ANHYDRIDE BY GAS PHASE OXIDATION OF O-XYLENE

This application is a national phase of PCT/EP2007/054841, filed on May 18, 2007 which claims priority to EP 06010415.5 filed May 19 2006, the entire contents of all are hereby incorporated by reference.

The present invention relates to a process for preparing phthalic anhydride by gas phase oxidation of o-xylene in a main reactor and a downstream postreactor.

The gas phase oxidation of o-xylene and/or naphthalene to phthalic anhydride (PA) is well known and described many times in the literature. A review is given, for example, by H. Suter, Phthalsäureanhydrid und seine Verwendung [Phthalic anhydride and its use], Steinkopf Verlag, Darmstadt 1972, or F. K. Towae, W. Enke, R. Jäckh, N. Bhargava in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A20, 1992, p. 181-190.

In general, the oxidation reaction of o-xylene is effected under air in a tube bundle reactor temperature-controlled with a salt melt. In this case, virtually complete conversion of the hydrocarbon used in the reactor and simultaneously a high product quality of the phthalic anhydride formed are desired. In order to achieve this on the one hand but simultaneously avoid damage to the catalyst as a result of high hotspot temperatures, catalysts of different activity are generally arranged layer by layer in the tubes, the less active catalyst generally being arranged in the fixed bed such that the reaction mixture comes into contact with it first, while the most active catalyst is disposed toward the gas outlet from the catalyst bed. Such activity structures of the catalyst are described, for example, by DE 198 23 262, DE 198 23 275, DE 100 40 827 and DE 102 06 989.

However, especially in the case of relatively high hydrocarbon loadings it becomes increasingly difficult to obtain sufficiently good product quality without yield losses in the reactor as a result of total oxidation to CO and CO_2, since the most active but least selective catalyst layer at the gas outlet of the catalyst bed here must make a relatively high contribution to the overall conversion. This effect also occurs over time as a result of the slow deactivation of the generally highly stressed selective layer or selective layers at the gas inlet of the catalyst bed.

One means of overcoming the above-described difficulties consists in the use of two separate reactors instead of a single reactor. For example, DE 20 05 969 describes a process for preparing phthalic anhydride in two separate reactors. The first reactor is a salt bath-cooled and largely isothermically operated tube bundle reactor, while the second reactor is an adiabatically operated shaft furnace. The reaction in the first reactor is conducted in such a way that from 1 to 20% by weight of the hydrocarbon used remains unchanged. The process is further characterized in that the temperature T_1 of the heat exchange medium in the first reactor is between 380 and 430° C. and the entrance temperature T_2 of the adiabatically operated second reaction stage obeys the relationship $T_2 = T_1 - 5$ to 150° C.

The process described in DE 198 07 018 and U.S. Pat. No. 5,969,160 comprises at least two separate reactors, the first reactor being a salt bath-cooled main reactor and the second reactor a postreactor without cooling equipment and with the same catalyst or a different catalyst. The product gas stream in the postreactor is from the top downward. The process enables the temperature in the main reactor to be lowered in the direction toward underoxidation conditions, which is why the phthalide values in the main reactor outlet and postreactor inlet are in the range from 0.5 to 0.9% by weight. These

conditions are controlled by the observation of the o-xylene content at the main reactor outlet and postreactor inlet which should explicitly be less than 100 ppm (0.01% by weight).

A further postreactor design is described in H.-J, Eberle, J. Breimair, H. Domes, T, Gutermuth, PTQ Summer 2000, 129-133. Here, a postreactor with a honeycomb catalyst is connected downstream of the salt bath-cooled tube bundle reactor which comprises a multilayer catalyst, the product stream being cooled to the desired entrance temperature by means of a product gas cooler before it enters the postreactor zone. The postreactor serves primarily to comply with a predetermined quality of the phthalic anhydride obtained, especially in the case of high o-xylene loadings and in the case of aged main reactor catalysts. The o-xylene concentration at the postreactor inlet, with a main reactor catalyst which has reached the end of its lifetime, is about 0.65-0.70% by weight of the sum of the organic components in the product gas stream, and the concentration of underoxidized secondary components such as phthalide or o-tolylaldehyde is 0.20-0.50% by weight of the sum of the organic components in the product gas stream.

It is an object of the invention to increase the total yield of phthalic anhydride without or without significant deterioration in the product quality.

The object is achieved by a process for preparing phthalic anhydride by catalytic gas phase oxidation of o-xylene, in which, in a main reactor, a gaseous mixture of o-xylene and an oxygenous gas is passed through at least two reaction zones whose temperature can be controlled independently, and converted to a gaseous intermediate reaction product which comprises unconverted o-xylene, phthalic anhydride underoxidation products and phthalic anhydride, and the intermediate reaction product is introduced into a postreactor, wherein the temperature of the reaction zones in the main reactor is regulated in such a way that the concentration of unconverted o-xylene in the intermediate reaction product is at least 0.5% by weight based on the total weight of the organic components in the intermediate reaction product.

Typically, the concentration of unconverted o-xylene in the intermediate reaction product is at least 0.6% by weight, preferably from 0.65 to 5% by weight, more preferably from 0.7 to 2.0% by weight.

The sum of the concentrations of the phthalic anhydride underoxidation products in the intermediate reaction product is preferably at least 0.5% by weight, based on the weight of the organic components in the intermediate reaction product. Phthalic anhydride underoxidation products are understood to mean C_6 species which have a lower oxidation state than phthalic anhydride and are oxidizable further to phthalic anhydride. These include in particular o-tolyladehyde, o-toluic acid and phthalide.

The sum of the concentrations of o-tolylaldehyde and phthalide in the intermediate reaction product is typically from 0.6 to 1.5% by weight, more preferably from 0.7 to 1.3% by weight.

The concentration of o-tolylaldehyde in the intermediate reaction product is preferably at least 0.25% by weight, in particular from 0.35 to 0.6% by weight.

The concentration of phthalide in the intermediate reaction product is preferably at least 0.25% by weight, in particular from 0.35 to 0.6% by weight.

The content of o-xylene in the intermediate reaction product is preferably less than or equal to 20 g/m^3 (STP), more preferably less than or equal to 15 g/m^3 (STP).

In preferred embodiments of the process according to the invention, measurements for the concentration of o-xylene in the intermediate reaction product are obtained continuously or at time intervals, for example at least once per week or at

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least once daily, and control interventions for the temperature of the reaction zones in the main reactor are formed from the measurements forms. For instance, the temperature of one or more or all of the reaction zones can be lowered if the concentration of o-xylene in the intermediate reaction product falls below a predefined target value or the inventive limiting value, or the temperature can be increased if the concentration of o-xylene in the intermediate reaction product is too high.

The concentration of o-xylene or phthalic anhydride underoxidation products, such as o-tolylaldehyde or phthalide, based on the weight of the organic components in the intermediate reaction product can be determined at ambient temperature (23° C.) by condensing all components of the intermediate reaction product which are condensible at this temperature and analyzing the condensate by means of gas chromatography in a suitable solvent such as acetone. Carbon monoxide and/or carbon dioxide which may be present in the intermediate reaction product do not count as organic components of the intermediate reaction product.

The reaction gas fed to the main reactor is generally obtained by mixing a gas which comprises molecular oxygen and, apart from oxygen, may also comprise suitable reaction moderators and/or diluents, such as steam, carbon dioxide and/or nitrogen, with o-xylene, and the oxygenous gas may generally comprise from 1 to 100 mol %, preferably from 2 to 50 mol % and more preferably from 10 to 30 mol % of oxygen, from 0 to 30 mol %, preferably from 0 to 10 mol % of steam, and from 0 to 50 mol %, preferably from 0 to 1 mol % of carbon dioxide, remainder nitrogen. The oxygenous gas is generally air.

The o-xylene loading of the gaseous mixture which enters the main reactor is generally from 30 g to 150 g per m³ (STP) of gas, preferably at least 60 g/m³ (STP), for example from 75 to 120 g/m³ (STP).

The main reactor used is preferably a salt bath-cooled tubular reactor which comprises at least two separate salt baths. Two (or more) sections of a tube bundle are flowed around by spatially separated heat carrier media in the form of a salt bath. The individual catalyst-filled tubes end in an upper tube plate and a lower tube plate. The tubes are conducted through at least one screen plate which divides the interior of the reactor into two or more zones for the heat carrier media. The reaction gas is generally passed from the top downward, i.e. in the direction of gravity, through the tube; however, a reverse flow direction is also conceivable. Assigned to each zone and spaced apart on the jacket of the reactor are annular channels through which the heat carrier medium can be drawn off from the reactor and fed back to the reactor after passing through a circulation pump. A substream of the circulated heat carrier medium is passed through a cooler in which, for example, saturated steam is produced. Guide plates may typically be present in the interior of the reactor, in order to impart a radial flow component to the heat carrier medium in the region of the tube bundle.

In preferred embodiments, the main reactor comprises two or three reaction zones, most preferably two reaction zones.

The temperature difference of the heat carrier medium between reactor inlet and outlet for the particular zone may be from 0.5 to 12° C., usually from 1 to 8° C. The heat carrier medium may, in relation to the reaction gas, pass through the tubular reactor either in cocurrent or in countercurrent in the particular zone.

The main reactor is typically operated with a temperature of the heat carrier medium of from 330 to 390° C. The gas temperature in the main reactor is in the range from 340 to 460° C., more preferably in the range from 370 to 435° C.

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The tube section over which the particular salt bath extends represents one reaction zone. Each reaction zone is filled with one catalyst or successive layers of different catalysts which are suitable tor the catalysis of the gas phase oxidation of o-xylene to phthalic anhydride. They are preferably coated or spherical catalysts, on whose core of an inert support material are applied one or more layers of catalytically active metal oxides.

In general, the reaction zones comprise catalysts of different activity, the reaction zone furthest downstream in flow direction of the gaseous mixture generally comprising one or more catalysts with higher activity than the reaction zone adjacent upstream. A catalyst bed should be considered to be present in that reaction zone to which it is assigned predominantly, i.e. to an extent of at least 60%, preferably at least 80%, of its longitudinal dimension.

In general, the reaction zone furthest downstream is operated at lower temperature than the reaction zone adjacent upstream, for example at a temperature of the heat carrier medium assigned to the particular reaction zone which is at least 2° C. lower, preferably at least 4° C. lower. The temperature at which a reaction zone is operated is regarded as the lowest temperature of the surrounding heat carrier medium.

The reaction zones may also comprise an identical catalyst, preferably a selective catalyst defined below.

Activity-structured catalyst beds, in which the catalysts placed toward the gas inlet side have an activity reduced in favor of a higher selectivity, are known, for example, from the patent documents mentioned at the outset. Selectivity is understood here to mean the selectivity with regard to the sum of phthalic anhydride and all C_8 species which are oxidizable further to phthalic anhydride. These catalysts placed toward the gas inlet side are frequently mimed to as "selective catalysts", in contrast to the "active catalysts" placed toward the gas outlet side.

The reaction zone(s) positioned furthest upstream in flow direction of the gaseous mixture and/or the reaction zone which adjoins the reaction zone furthest downstream in flow direction of the gaseous mixture in the upstream direction preferably comprise selective catalysts.

The reaction zone furthest downstream in flow direction of the gaseous mixture preferably composes at least one active catalyst.

Typical selective catalysts are

a) one or more catalysts whose active composition comprises a mixed multimetal oxide comprising silver, vanadium and if appropriate one or more promoter metals, in particular a silver vanadium oxide bronze,

b) one or more catalysts based on vanadium oxide and titanium dioxide, in which the alkali metal content of the active composition is greater than or equal to 0.12% by weight and the phosphorus content of the active composition (calculated as p) is less than or equal to 0.20% by weight, and

c) combinations of one or more catalysts according to the above definition a) and one or more catalysts according to the above definition b).

Typical active catalysts are catalysts based on vanadium oxide and titanium dioxide, in which the alkali metal content of the active composition is less than or equal to 0.20% by weight. Optionally, the active composition may also comprise phosphorus; for example, the phosphorus content of the active composition is greater than or equal to 0.12% by weight.

Mixed multimetal oxides which comprise silver, vanadium and if appropriate one or more promoter metals, and also silver vanadium oxide bronzes and their preparation, are

known per se, for example from WO 00/27753, WO 01/85337 and WO 2005/012216. Silver vanadium oxide bronzes are understood to mean silver vanadium oxide compounds with an atomic Ag:V ratio of less than 1. They are generally semiconductive or metallically conducting oxidic solids which preferably crystallize in layer or tunnel structures, the vanadium in the [V_2O_5] host lattice being present partly in reduced from to V(IV). Silver vanadium oxide bronzes form above 200° C., especially at temperatures of more than 300° C., by decomposition of the mixed multimetal oxides.

Suitable mixed multimetal oxides are, for example, those of the general formula I

$$Ag_{a-c}M^1_cV_2O_d{}^*e\ H_2O, \qquad\qquad I$$

in which

a is from 0.3 to 1.9,

M^1 is at least one metal selected from alkali metals and alkaline earth metals, Bi, Tl, Cu, Zn, Cd, Pb, Cr, Au, Al, Fe, Co, Ni, Mo, Nb, Ce, W, Mn, Ta, Pd, Pt, Ru and/or Rh.

c is from 0 to 0.5, with the proviso that (a-c) is $\geqq 0.1$,

d is a number which is determined by the valency and frequency of the elements other than oxygen in the formula I, and

e is from 0 to 20, preferably from 0 to 5.

In the multimetal oxide of the formula I, the variable A is preferably from 0.5 to 1.0 and more preferably from 0.6 to 0.9, the variable b is preferably from 0 to 0.1, and the variable c is preferably from 0.005 to 0.2, in particular from 0.01 to 0.1.

The number d is determined from the valency and frequency of the elements other than oxygen in the multimetal oxide of the formula I. The number e, which is a measure of the water content, is preferably from 0 to 5.

M^1 is preferably Na, K, Rb, Tl, Ni, W, Co, Fe, Mo, Nb, Zn, Ce and Mn.

Particular preference is given to multimetal oxides of the general formula Ia

$$Ag_aV_2O_d{}^*e\ H_2O, \qquad\qquad Ia$$

in which

a is from 0.6 to 0.9,

d is as defined above, and

e is from 0 to 5.

To prepare the multimetal oxides, a suspension of vanadium pentoxide (V_2O_5) is generally heated with the solution of a silver compound and, if appropriate, a solution of a compound of the metal component M^1 and a compound of Q. The solvent used for this reaction is preferably water. The silver salt used is preferably silver nitrate; the use of other soluble silver salts, for example silver acetate, silver perchlorate or silver fluoride, is likewise possible.

The salts of the metal component M^1 selected are generally those which are soluble in the solvent used. When water is used as the solvent in the preparation of the inventive multimetal oxides, it is possible, for example, to use the perchlorates or carboxylates, especially the acetates, of the metal component M^1. Preference is given to using the nitrates of the metal component M^1 in question.

According to the desired chemical composition of the multimetal oxide of the formula I, it is prepared by reacting the amounts of V_2O_5, silver compound and the compound of the metal component M^1 which are calculated from a and c of formula I with one another. The multimetal oxide thus formed can be isolated from the reaction mixture and stored until further use. Particularly advantageously, the isolation of the

resulting multimetal oxide suspension is performed by means of spray-drying. The spray-dried powder is then applied to an inert support.

Catalysts based on vanadium oxide and titanium dioxide comprise vanadium pentoxide in addition to titanium dioxide (in the form of its anatase modification). Typical catalysts based on vanadium oxide and titanium dioxide and their preparation are described in DE 198 23 262.

The catalyst based on vanadium oxide and titanium dioxide in the calcined state preferably comprises from 1 to 20% by weight of vanadium oxide, calculated as V_2O_5, and from 80 to 99% by weight of titanium dioxide calculated as TiO_2. In addition, small amounts of a multitude of other oxidic compounds may be present, which, as promoters, influence the activity and selectivity of the catalysts. The activity-reducing and selectivity-increasing promoters used are generally alkali metals such as cesium, lithium, potassium and rubidium, and especially cesium.

The activity-increasing additives used are generally phosphorus compounds, in the selective catalysts, at most small additions, if any, of phosphorus compounds are used.

The catalysts based on vanadium oxide and titanium dioxide may also comprise antimony compounds.

The components are used in the form of their oxides or in the form of compounds which are converted to oxides in the course of heating, or in the course of heating in the presence of oxygen. The vanadium components used may be vanadium oxides or vanadium compounds which are converted to vanadium oxides in the course of heating, individually or in the form of their mixtures. Preference is given to using V_2O_5 or NH_4VO_3, it is also possible to additionally use a reducing agent, such as formic acid or oxalic acid, in order to reduce the vanadium(V) compound at least partly to vanadium(IV). Suitable promoter (precursor) compounds are the corresponding oxides, or compounds which are converted to oxides after heating, such as sulfates, nitrates, carbonates. Suitable examples are Na_2CO_3, K_2O, Cs_2O, Cs_2CO_3, Cs_2SO_4, P_2O_5, $(NH_4)_2HPO_4$, Sb_2O_3.

The active composition is formed generally by preparing an aqueous slurry of the compound of the vanadium component, of the titanium dioxide and of promoter (precursor) compounds in suitable amounts, and stirring the slurry until sufficient homogenization is achieved. The slurry can then be spray-dried or be used as such for the coating.

The catalysts used in the process according to the invention are generally coated catalysts in which the catalytically active composition is applied in coating form on an inert support. The layer thickness of the catalytically active composition is generally from 0.02 to 0.2 mm, preferably from 0.05 to 0.1 mm. In general, the catalysts have an active composition layer with essentially homogeneous chemical composition applied in coating form.

The inert support materials used may be virtually all known support materials, for example quartz (SiO_2), porcelain, magnesium oxide, tin dioxide, silicon carbide, rutile, alumina (Al_2O_3), aluminum silicate, steatite (magnesium silicate), zirconium silicate, cerium silicate or mixtures of these support materials. The support material is generally nonporous. Advantageous support materials which should be emphasized are in particular steatite and silicon carbide. The shape of the support material is generally uncritical. For example, catalyst supports can be used in the form of spheres, rings, tablets, spirals, tubes, extrudates or spall. The dimensions of these catalyst supports correspond to those of catalyst supports typically used to prepare coated catalysts for the gas phase partial oxidation of aromatic hydrocarbons. Preference is given to using steatite in the form of spheres having a

diameter of from 3 to 6 mm or of rings having an external diameter of from 5 to 9 mm and a length of from 4 to 7 mm.

The active composition layer can be applied to the support by any methods known per se, for example by spraying solutions or suspensions in a coating drum, or coating with a solution or suspension in a fluidized bed. If is possible for organic binders, preferably copolymers, advantageously in the form of an aqueous dispersion, of vinyl acetate/vinyl laurate, vinyl acetate/acrylate, styrene/acrylate, vinyl acetate/maleate, vinyl acetate/ethylene and hydroxyethylcellulose to be added to the catalytically active composition, the amounts of binder used advantageously being from 3 to 20% by weight, based on the solids content of the solution of the active composition constituents. The binders applied burn off within a short time after the introduction of the catalyst and startup of the reactor. The binder addition additionally has the advantage that the active composition adheres efficiently on the support, so as to facilitate transport and filling of the catalyst.

The gaseous intermediate reaction product which leaves the main reactor is fed to a postreactor. It forms the exclusive feed to the postreactor, i.e. no gases, such as fresh or waste air or o-xylene, are added to the intermediate reaction product.

Useful postreactors are all reactors which are suitable for performing heterogeneously catalyzed gas phase reactions, especially fixed bed reactors with a fixed catalyst bed, tube bundle reactors, reactors with catalyst-coated monolithic honeycombs and the like. They may be vertical or horizontal designs; the flow toward vertical reactors may be from the bottom or from the top.

It is usually preferred that the intermediate reaction product which leaves the main reactor is cooled by means of a suitable cooling stage before it enters the postreactor. The difference between the exit temperature from the main reactor and the entrance temperature into the postreactor is preferably at least 5° C., in particular at least 10° C. The performance of the cooling stage is appropriately controlled as a function of the o-xylene concentration in the intermediate reaction product and the activity of the postreactor catalyst such that the phthalic anhydride yield and purity are maximized.

The main reactor, the cooling stage and the postreactor may be arranged in separate apparatus. Suitable cooling stages are liquid-cooled indirect heat exchangers or gas-gas heat exchangers, by means of which the reaction gas fed to the main reactor can be preheated.

Alternatively, it is also possible to combine main reactor and cooling stage, or cooling stage and postreactor, in a single apparatus. For example, the cooling stage can be designed as an immediate extension of the reaction tubes of the main reactor, which, in the region of the cooling stage, are not filled with catalyst and are cooled by means of a separate circuit of a heat carrier medium or with a substream of the heat carrier medium coming from the cooler.

It is also possible for the functions of the main reactor, of a cooling stage and of the postreactor to be arranged in a single casing, as described in DE 101 44 857.

The design of the postreactor depends upon its operating mode. In one possible embodiment, the postreactor is operated essentially adiabatically.

In another possible embodiment, at least some of the heat of reaction which arises in the postreactor is removed by indirect cooling with a heat carrier medium. Suitable heat carrier media for the postreactor are heat carrier oils, salt melts, air or water. Typical cooling processes can be found in the patent application DE 10 2004 061770 which has an earlier priority date than the present application. Particular

preference is given to a design in which the reaction gas flows first through an adiabatic catalyst layer and then through a catalyst layer disposed between thermoplates.

The postreactor catalysts used are preferably coated or spherical catalysts, on whose core of an inert support material are applied one or more layers of catalytically active metal oxides. Typical support materials and typical metal oxides and promoters used can be found in DE 198 23 262. Preference is given to using catalysts which are different form the catalysts used in the main reactor. Preference is given to using, in the postreactor, a catalyst based on vanadium oxide and titanium dioxide, in which the alkali metal content of the active composition is less than or equal to 0.20% by weight. Optionally, the active composition comprises phosphorus; the phosphorus content of the active composition is, for example, greater than or equal to 0.12% by weight.

The postreactor is typically operated at gas temperatures of from 240 to 360° C., more preferably from 270 to 350° C. The highest gas temperature which occurs in the postreactor is preferably at least 30° C. lower, preferably at least 40° C. lower, and the highest gas temperature which occurs in the main reactor.

In general, the reaction gas which leaves the postreactor is cooled in a product gas condenser and the phthalic anhydride is deposited out of the hot reaction gases in a customary manner by means of phthalic anhydride separators operated in alternation. Optionally, a so-called liquid separator can be connected upstream of the separators, which is advantageous particularly at high loadings.

The process according to the invention can also be applied to the preparation of other products by catalytic gas phase oxidation, for example phthalic anhydride from naphthalene or o-xylene/naphthalene mixtures, acrylic acid from propone, maleic anhydride from benzene, butane, butane or butadiene, benzoic acid from toluene, etc.

The invention is illustrated in detail by the examples and comparative examples which follow.

EXAMPLES

Preparation of the Catalysts
Preparation of the Main Reactor Catalyst I (Selective Catalyst)

After stirring for 18 hours, 236.6 g of a suspension consisting of 104.9 g of oxalic acid, 39.4 g of vanadium pentoxide, 17.0 g of antimony oxide, 2.87 g of cesium sulfate, 3.15 g of ammonium dihydrogenphosphate, 149.0 g of formamide, 465.9 g of titanium dioxide of the anatase modification having a BET surface area of 20 m^2/g, and 721.0 g of water are applied in a coating drum at 160° C. together with 13.0 g of organic binder to 1400 g of steatite rings of dimensions 8×6×5 mm (external diameter×height×internal diameter), in a second step, the rings thus coated are coated with 236.2 g of a second suspension which had likewise been stirred beforehand for 18 h, consisting of 56.7 g of oxalic add, 21.0 g of vanadium pentoxide, 2.87 g of cesium sulfate, 198.0 g of formamide, 501.9 g of titanium dioxide and 720.3 g of water, together with 12.8 g of organic binder.

After calcination of the catalyst at 450° C. for one hour, the active composition applied to the steatite rings is 9.3%. The active composition has the composition of 5.75% V$_2$O$_5$, 1.6% Sb$_2$O$_3$, 0.40% Cs, 0.08% P, remainder TiO$_2$.

Preparation of the Main Reactor Catalyst II (Active Catalyst)

After stirring for 18 hours, 538.0 g of a suspension consisting of 106.4 g of oxalic acid, 39.4 g of vanadium pentoxide, 17.0 g of antimony oxide, 0.63 g of cesium sulfate, 3.35 g of ammonium dihydrogenphosphate, 149.6 g of forma-

mide, 467.5 g of titanium dioxide of the anatase modification having a BET surface area of 20 m²/g, and 719.1 g of water are applied in a coating drum at 160° C. to 1400 g of steatite rings of dimensions 8×6×5 mm (external diameter×height× internal diameter).

After calcination of the catalyst at 450° C. for one hour, the active composition applied to the steatite rings is 10.5%. The active composition has the composition of 7.5% V_2O_5, 3.2% Sb_2O_5, 0.09% Cs, 0.17% P, remainder TiO_2.

Preparation of the Postreactor Catalyst

After stirring for 18 hours, 540.2 g of a suspension consisting of 105.5 g of oxalic acid, 39.4 g of vanadium pentoxide, 17.0 g of antimony oxide, 0.29 g of cesium sulfate, 8.9 g of ammonium dihydrogenphosphate, 149.0 g of formamide, 467.0 g of titanium dioxide of the anatase modification having a BET surface area of 20 m²·g⁻¹, and 720.5 g of water are applied in a coating drum at 160° C. to 1400 g of steatite rings of dimensions 8×6×5 mm (external diameter×height×internal diameter).

After calcination of the catalyst at 450° C. for one hour, the active composition applied to the steatite rings is 10.6%. The active composition has the composition of 7.5% V_2O_5, 3.2% Sb_2O_3, 0.04% Cs, 0.41% P, remainder TiO_3.

Examples 1 to 7

The main reactor used was a tube bundle reactor with 99 normal tubes and 2 thermal tubes. The normal tubes had an internal width of 25 mm, the thermal tubes an internal width of 29 mm with sleeves (diameter 10 mm) with installed 30-point multi-element with temperature measuring points at a distance of 10 cm or with a sampling element according to DE 101 10 847. From the bottom upward, 101 cm of main reactor catalyst II and then 229 cm of main reactor catalyst I were introduced into each of the 360 cm-long iron tubes. By means of pressure equalization, it was ensured that the same inlet pressure was present at each tube inlet. If appropriate, a little main reactor catalyst I was added or sucked out in the 99 normal tubes; in the two thermal tubes, the pressure equalisation was achieved by adding inert material in the form of steatite spheres and quartz chips. For temperature control, the iron tubes were surrounded by a salt melt which was disposed in two separate salt baths. The lower salt bath (salt bath B) surrounded the tubes from the lower tube plate up to a height of 140 cm; the upper salt bath (salt bath A) surrounded the tubes from the height of 140 cm up to the upper tube plate.

The postreactor (internal diameter 45 cm, height about 100 cm) was equipped at a height of about 90 cm with cooling coils (diameter 12 mm, cooling coil separation about 30 mm) which were charged in the lower part with air at ambient temperature as the cooling medium. The postreactor was filled with postreactor catalyst up to a fill height of 65 cm.

To operate the plant, an air/o-xylene mixture was passed from the top downward through the reactor at main reactor inlet temperature about 200-205° C., then cooled to a certain postreactor inlet temperature in a heat exchanger and then passed from the top downward through the postreactor. The o-xylene used had a purity of 98.5-99.0% by weight. The air cooling in the lower part of the postreactor was effected over a height of 47 cm (examples 1, 4, 6 and 7) or 53 cm (examples 2, 3 and 5) such that a certain temperature in the catalyst bed, which was measured 10 cm above the postreactor outlet, was established.

After a generally customary runup time of the main reactor catalyst, the results reported in table 1 were obtained.

Example 8

The experiment was performed in a manner corresponding to that specified under examples 1 to 7, except that the postreactor was operated adiabatically, i.e. no air was passed through the cooling coils. The results are reproduced in table 1.

Comparative Examples 1 to 9

The experiment was performed in the manner corresponding to that specified under examples 1 to 7, except that the postreactor was operated adiabatically and the two salt baths of the main reactor were operated at essentially the same temperature. The results are reproduced in table 2.

In the tables:

run day=operating day from the first startup of the main reactor catalyst;

salt bath A=salt bath temperature of the salt bath placed toward the reactor inlet;

salt bath B=salt bath temperature of the salt bath placed toward the reactor outlet;

o-xylene MR outlet, o-tolylaldehyde MR outlet and phthalide MR outlet=o-xylene, o-tolylaldehyde and phthalide content respectively in % by weight of the organic components of the crude product gas at the main reactor outlet;

o-xylene PR outlet, o-tolylaldehyde PR outlet and phthalide PR outlet=o-xylene, o-tolylaldehyde and phthalide content respectively in % by weight of the organic components of the crude product gas at the postreactor outlet;

PA yield PR outlet=PA yield in % by weight based on 100% o-xylene from the analysis of the crude product gas in the postreactor outlet.

TABLE 1

Results of examples 1 to 8									
Compara-tive example	Run day	o-Xylene [g/m³ (STP)]	Air (m³ (STP)/h per tube]	Temperature of Salt bath A Salt bath B [° C.]	Temperature of PR inlet Cat. Bed [° C.]	o-Xylene MR outlet PR outlet [% by wt.]	o-Tolylaldehyde MR outlet PR outlet [% by wt.]	Phthalide MR outlet PR outlet [% by wt.]	PA yield PR outlet [m/m %]
1	231	80.0	3.8	345.5	320	0.77	0.38	0.41	115.7
				340.1	290	0.02	0.05	0.09	
2	323	80.0	3.8	345.6	320	0.73	0.37	0.40	115.8
				340.1	291	0.03	0.05	0.09	
3	233	80.0	3.8	345.6	324	0.67	0.34	0.38	115.5
				338.9	291	0.02	0.04	0.08	
4	235	80.0	3.8	345.6	320	0.85	0.39	0.41	115.4
				339.1	292	0.02	0.05	0.09	
5	238	80.0	3.8	345.6	324	0.76	0.37	0.40	115.5
				339.0	289	0.03	0.05	0.10	
6	253	80.0	3.8	345.6	320	1.08	0.47	0.50	116.3
				339.0	296	0.04	0.06	0.13	

TABLE 1-continued

Results of examples 1 to 8

Comparative example	Run day	o-Xylene [g/m³ (STP)]	Air (m³ (STP)/h per tube]	Temperature of Salt bath A Salt bath B [°C.]	Temperature of PR inlet Cat. Bed [°C.]	o-Xylene MR outlet PR outlet [% by wt.]	o-Tolylaldehyde MR outlet PR outlet [% by wt.]	Phthalide MR outlet PR outlet [% by wt.]	PA yield PR outlet [m/m %]
7	255	80.0	3.8	345.6	320	0.67	0.34	0.37	115.7
				338.5	295	0.01	0.03	0.05	
8	240	80.0	3.8	345.5	320	1.09	0.46	0.49	115.3
				339.0	340	0.01	0.02	0.04	

TABLE 2

Results of comparative examples 1 to 9

Example	Run day	o-Xylene [g/m³ (STP)]	Air [m³ (STP)/h per tube]	Temperature of Salt bath A Salt bath B [°C.]	Temperature of PR inlet Cat. Bed [°C.]	o-Xylene MR outlet PR outlet [% by wt.]	o-Tolylaldehyde MR outlet PR outlet [% by wt.]	Phthalide MR outlet PR outlet [% by wt.]	PA yield PR outlet [m/m %]
1	148	60.5	3.8	354.0	284	0.02	0.02	0.01	113.4
				353.9	287	0.01	0.01	0.00	
2	151	63.5	3.8	351.0	284	0.00	0.03	0.03	114.2
				351.0	287	0.01	0.01	0.00	
3	154	71.0	3.8	348.0	284	0.02	0.05	0.06	114.5
				348.0	287	0.01	0.02	0.01	
4	156	76.8	3.8	346.0	284	0.05	0.09	0.11	114.3
				348.0	287	0.00	0.03	0.02	
5	157	80.0	3.8	345.0	284	0.10	0.14	0.17	114.1
				345.1	268	0.00	0.04	0.06	
6	226	80.0	3.8	345.7	293	0.01	0.02	0.02	114.2
				345.8	291	0.00	0.02	0.01	
7	247	80.0	3.8	346.5	274	0.10	0.11	0.14	114.9
				346.5	280	0.00	0.02	0.03	
8	248	80.0	3.8	346.5	274	0.10	0.11	0.14	114.6
				346.5	280	0.00	0.02	0.02	
9	270	79.9	3.8	346.7	274	0.07	0.09	0.13	114.5
				346.7	280	0.00	0.02	0.02	

The invention claimed is:

1. A process for preparing phthalic anhydride by catalytic gas phase oxidation of o-xylene, wherein, in a main reactor, a gaseous mixture of o-xylene and an oxygenous gas is passed through at least two reaction zones whose temperature can be controlled independently, and converted to a gaseous intermediate reaction product which comprises unconverted o-xylene, phthalic anhydride underoxidation products and phthalic anhydride, and the intermediate reaction product is introduced into a postreactor, wherein the temperature of the reaction zones in the main reactor is regulated in such a way that the concentration of unconverted o-xylene in the intermediate reaction product is at least 0.5% by weight, based on the weight of the organic components in the intermediate reaction product,

    wherein the reaction zone furthest downstream is operated at lower temperature than the reaction zone adjacent upstream, and

    wherein the concentration of o-tolylaldehyde in the intermediate reaction product is at least 0.25% by weight.

2. The process according to claim 1, wherein the sum of the concentrations of phthalic anhydride underoxidation products in the intermediate reaction product is at least 0.5% by weight.

3. The process according to claim 1, wherein the sum of the concentrations of o-tolylaldehyde and phthalide is at least 0.5% by weight.

4. The process according to claim 1, wherein the concentration of o-tolylaldehyde in the intermediate reaction product is at least 0.25% by weight.

5. The process according to claim 1, wherein the concentration of phthalide in the intermediate reaction product is at least 0.25% by weight.

6. The process according to claim 1, wherein the reaction zones comprise catalysts of different activity.

7. The process according to claim 6, wherein the reaction zone furthest downstream in flow direction of the gaseous mixture comprises a catalyst of higher activity than the reaction zone adjacent upstream.

8. The process according to claim 6, wherein the reaction zone furthest downstream in flow direction of the gaseous mixture comprises at least one catalyst based on vanadium oxide and titanium dioxide, in which the alkali metal content of the active composition is less than or equal to 0.20% by weight.

9. The process according to claim 6, wherein the reaction zone which adjoins the reaction zone furthest downstream in flow direction of the gaseous mixture in upstream direction comprises catalysts which are selected from

    a) one or more catalysts whose active composition comprises a mixed multimetal oxide comprising silver, vanadium and optionally one or more promoter metals,

    b) one or more catalysts based on vanadium oxide and titanium dioxide, in which the alkali metal content of the active composition is greater than or equal to 0.12% by

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weight and the phosphorus content of the active composition is less than or equal to 0.20% by weight, or

c) a combination of one or more catalysts according to the above definition a) and one or more catalysts according to the above definition b).

10. The process according to claim **1**, wherein measurements for the concentration of o-xylene are obtained in the intermediate reaction product and control interventions for the temperature of the reaction zones in the main reactor are formed from the measurements.

11. The process according to claim **1**, wherein the o-xylene loading of the gaseous mixture which enters the main reactor is at least 60 g/m^3 (STP).

12. The process according to claim **1**, wherein at least some of the heat of reaction which arises in the postreactor is removed by indirect cooling with a heat carrier medium.

13. The process according to claim **1**, wherein the postreactor is operated essentially adiabatically.

14. The process according to claim **1**, wherein the intermediate reaction product which leaves the main reactor is cooled before it enters the postreactor.

15. The process according to claim **2**, wherein the sum of the concentrations of o-tolylaldehyde and phthalide is at least 0.5% by weight.

16. The process according to claim **2**, wherein the concentration of phthalide in the intermediate reaction product is at least 0.25% by weight.

17. The process according to claim **3**, wherein the concentration of phthalide in the intermediate reaction product is at least 0.25% by weight.

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